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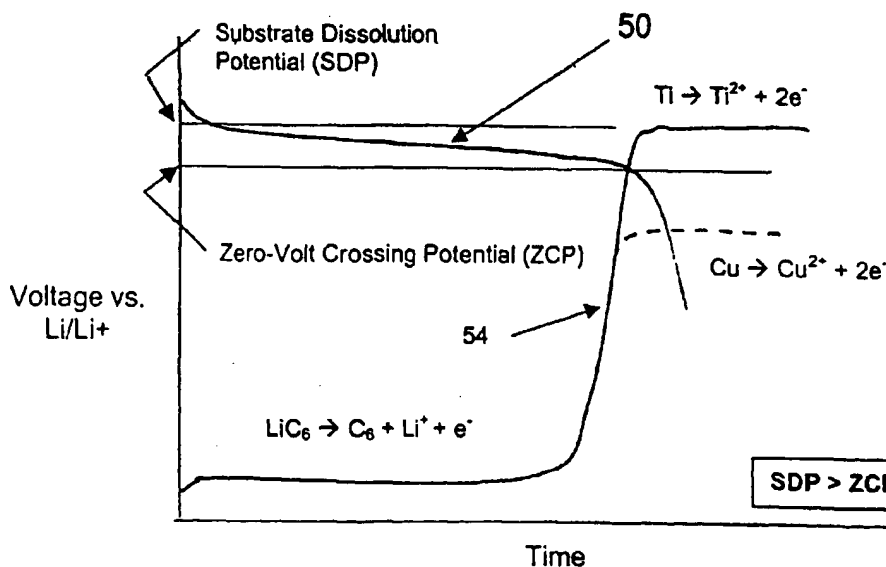
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(54) Title: LITHIUM ION BATTERY CAPABLE OF BEING DISCHARGED TO ZERO VOLTS



(57) Abstract: A lithium ion battery particularly configured to be able to discharge to a very low voltage, e.g. zero volts, without causing permanent damage to the battery. More particularly, the battery is configured to define a Zero Volt Crossing Potential (ZCP) which is lower than a Substrate Dissolution Potential (SDP) to thus avoid low voltage substrate damage.

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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

**TITLE : LITHIUM ION BATTERY CAPABLE OF BEING
DISCHARGED TO ZERO VOLTS**

RELATED APPLICATIONS

5 This application claims the benefit of U.S. Provisional Application
60/199895 filed April 26, 2000.

FIELD OF THE INVENTION

This invention relates generally to rechargeable batteries and more
10 particularly to a rechargeable lithium battery capable of discharging to zero volts
without causing damage to the battery.

BACKGROUND OF THE INVENTION

Rechargeable lithium batteries are widely discussed in the literature and
15 are readily commercially available. They typically consist of a positive electrode
and a negative electrode spaced by a separator, an electrolyte, a case, and
feedthrough pins respectively connected to the electrodes and extending
externally of the case. Each electrode is typically formed of a metal substrate
that is coated with a mixture of an active material, a binder, and a solvent. In a
20 typical battery design, the electrodes comprise sheets which are rolled together,
separated by separator sheets, and then placed in a prismatic case. Positive
and/or negative feed through pins (i.e., terminals) are then connected to the
respective electrodes and the case is sealed.

The negative electrode is typically formed of a copper substrate carrying
25 graphite as the active material. The positive electrode is typically formed of an
aluminum substrate carrying lithium cobalt dioxide as the active material. The
electrolyte is most commonly a 1:1 mixture of EC:DEC in a 1.0 M salt of LiPF₆.
The separator is frequently a micro porous membrane made of a polyolephine,
such as a combination of polyethylene and/or polypropylene which can, for
30 example, be approximately 25µm thick.

It is typical to use protection circuitry with lithium ion batteries to avoid
potential deleterious effects. Thus, protection circuitry is frequently employed

to terminate charging if the voltage or temperature of the battery(or any cell) exceeds a certain level. Moreover, it is common to incorporate a low voltage cutoff to disconnect the battery from its load if the voltage of the battery (or any cell) falls below a certain lower level. This latter precaution is taken to prevent
5 permanent damage to the battery which can occur if a voltage greater than a Damage Potential Threshold (DPT) is applied to one of the electrodes. For example, corrosion or decomposition of the negative electrode substrate can occur if a voltage greater than a Substrate Dissolution Potential (SDP) is applied to the negative electrode.

10

SUMMARY OF THE INVENTION

The present invention is directed to a rechargeable lithium ion battery particularly configured to be able to discharge to a very low voltage, e.g. zero volts, without causing permanent damage to the battery. More particularly, a
15 battery in accordance with the invention is configured to define a Zero Volt Crossing Potential (ZCP) which is lower than the battery's Damage Potential Threshold (DPT) and more specifically its Substrate Dissolution Potential (SDP), to thus avoid low voltage substrate damage.

The ZCP refers to the voltage of each of the electrodes relative to a
20 lithium reference (Li/Li^+) when the battery potential, i.e., the potential between the electrodes, is zero. The SDP refers to the dissolution potential of the negative electrode substrate relative to the lithium reference (Li/Li^+). A conventional lithium ion battery typically exhibits a ZCP of about 3.6 volts which can slightly exceed the battery's SDP.

25 In accordance with the present invention, the material selected for the negative electrode substrate has a dissolution potential greater than the ZCP. Commercially pure titanium and titanium alloys are preferred. Nickel, nickel alloys, and stainless steel can also be used.

In the normal operation of a lithium ion battery, a solid electrolyte
30 interface (SEI) layer, i.e., a passivation layer, is formed on the negative electrode, attributable to a reaction between the negative electrode and the electrolyte. The SEI layer comprises an insulating membrane that tends to

inhibit the continuing reaction of the negative electrode and electrolyte. It has been recognized that this SEI layer can dissolve at a voltage above a certain level, i.e., Film Dissolution Potential (FDP), which can lead to permanent damage to the negative electrode. In accordance with a preferred embodiment
5 of the invention, the battery is configured to assure a ZCP lower than said FDP.

A battery's ZCP level relative to the lithium reference is dependent in part on the materials used for the positive and/or negative electrodes. In accordance with a preferred embodiment of the invention, a positive electrode active material, e.g., $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ ($0 < x \leq 1$), is selected which exhibits a discharge curve
10 appropriate to achieve a relatively low ZCP level. This feature of the preferred embodiment facilitates the implementation of a battery in accordance with the invention characterized by a Zero Crossing Potential (ZCP) less than its Substrate Dissolution Potential (SDP) and/or its Film Dissolution Potential (FDP).

15 Batteries in accordance with the present invention are particularly suited for use in critical applications where physical access to the battery may be difficult. For example, batteries in accordance with the invention find application in medical devices configured to be implanted under the skin in a patient's body. Such a medical device is typically comprised of a hermetically sealed housing
20 formed of biocompatible material and dimensioned sufficiently small as to be able to be implanted without interfering with normal bodily function. A battery in accordance with the invention includes a case configured for mounting in the device housing. The battery case can be of a variety of shapes, e.g., prismatic or cylindrical, and typically defines a volume of between .05 cc and 30 cc.
25 Batteries within this range exhibit capacities between 1.0 milliamp hours and 3 amp hours. An exemplary battery for use in such a device includes a prismatic hermetically sealed battery casing having dimensions of 35 mm x 17mm x 5.5 mm. The device is intended to be implanted in the lower back region to help alleviate back pain using neurostimulation techniques.

30

BRIEF DESCRIPTION OF THE DRAWINGS

The above and other features and uniqueness of the invention will be better visualized from the following drawings and schematics.

Figure 1A schematically depicts positive and negative battery electrodes
5 rolled around a mandrel for placement in a battery case and Figure 1B depicts in cross-section a complete battery;

Figure 2 shows a typical deep discharge curve for a conventional lithium ion battery using copper as the negative electrode substrate and lithium cobalt dioxide LiCoO_2 as the positive electrode active material;

10 Figure 3 shows a typical deep discharge curve for a zero volt battery in accordance with the present invention using titanium as the negative electrode substrate;

Figure 4 shows a typical deep discharge curve for a zero volt battery in accordance with the present invention using $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ ($0 < x \leq 1$) as the positive
15 electrode active material;

Figure 5 is a table showing preliminary test results of various battery configurations in accordance with the present invention; and

Figure 6 schematically depicts a battery in accordance with the invention contained within an implantable medical device housing.

20

DETAILED DESCRIPTION

The following description discloses presently contemplated preferred embodiments for practicing the invention. This description is not to be taken in a limited sense, but is offered for the purpose of describing the preferred modes
25 of the invention. The scope of the invention should be determined with reference to the claims.

Figures 1A and 1B schematically depict a typical lithium ion battery construction 10 comprising a prismatic case 12 containing a positive electrode 14 and a negative electrode 16, rolled around a mandrel 18. Separator sheets
30 20, 22 are incorporated in the rolling to electrically separate the electrodes. The case 12 also typically includes electrolyte material (not shown) and positive and

negative feed through pins (i.e., terminals) 26, 28 which are respectively connected to the electrodes 14, 16 and extend externally of the case 12.

The positive electrode 14 is typically comprised of a thin metal substrate, e.g., aluminum, carrying a layer of positive active material, e.g., lithium cobalt 5 dioxide LiCoO_2 mixed with a binder, and coated on both faces of the substrate. The negative electrode 16 is typically comprised of a thin metal substrate, e.g., copper, carrying a layer of negative active material, e.g., graphite coated on both faces of the substrate.

Two layers of separator 20, 22 electrically separate the electrodes 14, 16 10 from each other, enabling the electrodes to be rolled around mandrel 18. Each separator layer can comprise a micro porous membrane made of a combination of polypropylene and is approximately $25\mu\text{m}$ thick. The electrolyte is most commonly a 1:1 mixture of EC:DEC in a 1.0 M salt of LiPF_6 .

Figure 2 shows typical deep discharge performance curves for a 15 conventional lithium ion battery. The y-axis represents voltage relative to a lithium reference (Li/Li^+) or counter electrode and the x-axis represents time. Curves 50 and 52 respectively depict the discharge curves for the positive and negative electrodes. The battery output voltage is the difference between the positive electrode voltage and the negative electrode voltage. During discharge, 20 the positive electrode voltage decreases relative to Li/Li^+ and the negative voltage increases, primarily near the end of discharge. Typically, a protection or management circuit stops the discharge when the battery voltage reaches 2.5 Volts. If the management circuit does not stop the discharge, the negative electrode potential will rise until it reaches the potential of the positive electrode 25 which constitutes the Zero Volt Crossing Potential (ZCP) and is typically about 3.6 volts in conventional lithium ion battery constructions. The negative electrode potential at ZCP, relative to Li/Li^+ , can exceed the dissolution potential of the negative electrode substrate (SDP), e.g., 3.3volts for copper, and cause dissolution and permanent damage to the substrate. The present invention is 30 directed to battery improvements to assure that the value of SDP is greater than the value of ZCP, as represented in Figure 3.

Figure 3 depicts deep discharge performance curves for a lithium ion battery in accordance with the present invention in which the negative electrode substrate is formed of titanium instead of copper. The use of titanium increases the knee of the negative electrode curve 54 to position the SDP above the ZCP. This relationship considerably reduces potential damage to the negative electrode substrate. In addition to commercially pure titanium, i.e., titanium CP, other materials can be used to raise the SDP sufficiently, e.g. titanium alloys, nickel, nickel alloys, and stainless steel.

Figure 3 demonstrates how the SDP level can be increased relative to the ZCP by proper choice of the negative electrode substrate material. Alternatively, or additionally, the ZCP level can be decreased relative to the SDP by proper choice of the positive electrode active material, as depicted in Figure 4.

More particularly, Figure 4 shows the discharge curve 60 for a positive electrode using lithium nickel cobalt dioxide $\text{LiNi}_x\text{Co}_{1-x}$ (where $0 < x \leq 1$) as the active material, i.e., as the intercalation compound. Note that the curve of Figure 4 exhibits a greater negative slope than the analogous curve 50 of Figure 2 representing the standard intercalation compound LiCoO_2 . The effect of the increased negative slope is to lower the ZCP level relative to the lithium reference and the SDP. As was the case in connection with Figure 3, this reduces the potential damage to the negative electrode substrate. Additionally, however, the ZCP level also falls below a Film Dissolution Potential (FDP) which is the voltage above which a solid electrolyte interface (SEI) layer begins to dissolve. The SEI, or film, comprises a passivation layer which forms on the negative electrode and functions to inhibit a continuing reaction between the negative electrode active material and the electrolyte. Dissolution of the SEI can noticeably damage the negative electrode active material.

Experiments have been performed at two different temperatures employing the aforescribed techniques depicted in Figures 3 and 4. The preliminary results are summarized in the table of Figure 5. Four different battery configurations were constructed as shown. Configuration (1) corresponds to the conventional arrangement represented in Figure 2

comprising a copper substrate for the negative electrode and LiCoO_2 for the positive active material. The battery was built and then recycled once to get an initial capacity measurement. The battery was then shorted between the positive and negative leads to achieve a zero volt state. This zero volt condition
5 was held for one week and then recharged and discharged to get a capacity measurement after zero-volt storage. The capacity retention is calculated by dividing the discharge capacity after zero volt storage by the initial capacity and multiplying by 100%. In this manner, this percentage reflects any damage that had occurred to the battery while in the zero volt state.

10 As represented in Figure 5, the capacity retention for battery configuration (1) is below 80%, thus suggesting that damage had been done to the battery. After opening the battery and examining the electrodes, it was seen that copper dissolution had occurred. This battery (1) configuration performed poorly at both temperature settings.

15 The battery configuration (2) used LiCoO_2 as the positive active material and a titanium substrate as the negative substrate corresponding to the arrangement represented in Figure 3. The results show that at 25°C the capacity retention was at about 98% after the zero volt condition. However, at a higher temperature (37°C), performance deteriorates to below 80%. This
20 suggests that perhaps the zero volt crossing potential was sufficiently below SDP to avoid substrate dissolution but still high enough to exceed FDP and cause damage to the negative electrode active material. Accordingly, attempts were made to lower ZCP further to avoid damage both to the negative active material and the negative electrode substrate.

25 The battery configuration (3) utilizes $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ ($0 < x \leq 1$) as the positive active material with copper negative electrode substrate. The results show that at 37°C the capacity retention is quite high at 90%. However, examination after the test, revealed that some copper dissolution occurred. Battery configuration (4) uses both $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ ($0 < x \leq 1$) as the positive active material and the
30 titanium as the negative electrode substrate material. Results show that this configuration gives the best capacity retention after zero volt storage.

From the foregoing table (Figure 5), it appears that a performance gain is achieved by configuration (2) using a titanium negative electrode substrate and by configuration (3) using lithium nickel cobalt dioxide as the positive active material. However, maximum performance gain appears in configuration (4) 5 which combines both of these features.

Figure 6 schematically depicts a battery 60 in accordance with the invention mounted in a housing 64 (shown partially open for the purposes of illustration) of a medical device 66 configured for implanting in a patient's body. The housing 64 is preferably formed of biocompatible material and hermetically 10 sealed. The device 66 is typically used for monitoring and/or affecting body parameters. For example, the device can be used to electrically stimulate nerves. The casing 68 of battery 64 can, for example, have dimensions of 35 mm x 17 mm x 5.5 mm.

While the invention has been described with reference to specific 15 exemplary embodiments and applications, it should be recognized that numerous modifications and variations will occur to those skilled in the art without departing from the spirit and scope of the invention set forth in the appended claims.

CLAIMS

1. A rechargeable battery comprising:
a positive electrode;
a negative electrode
5 said positive electrode comprising a metal substrate having a lithium based active material formed thereon;
said negative electrode comprising a metal substrate having a lithium based active material formed thereon;
said positive and negative electrodes defining a Zero Volt
10 Crossing Potential (ZCP) relative to a reference level when the voltage between said electrodes is zero;
said negative electrode substrate being susceptible of permanent damage when a voltage potential exceeding a Substrate Dissolution Potential (SDP) is applied thereto; and wherein
15 said positive and negative electrodes are configured to establish ZCP at a lower level than SDP.
2. The battery of claim 1 wherein said negative electrode substrate is formed of a material from the group titanium and titanium alloy.
20
3. The battery of claim 1 wherein said negative electrode substrate is formed of stainless steel.
4. The battery of claim 1 wherein said negative electrode substrate
25 is formed of a material from the group nickel and nickel alloy.
5. The battery of claim 1 wherein said positive electrode active material comprises a lithium-nickel-cobalt compound, $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ where $0 < x \leq 1$.
30

6. The battery of claim 1 further including an electrolyte; and wherein
said negative electrode can react to said electrolyte to form a solid
electrolyte interface (SEI) layer, said SEI layer being susceptible of permanent
damage when a voltage potential exceeding a Film Dissolution Potential (FDP)
5 is applied thereto; and wherein
said positive and negative electrodes are configured to establish
ZCP at a lower level than FDP.
7. The battery of claim 1 further including a case for housing said
10 positive and negative electrodes; and wherein
said case is configured for implanting in a patient's body.
8. The battery of claim 7 wherein said case is hermetically sealed.
9. The battery of claim 7 wherein said case has a volume of less
15 then 30 cc.
10. A rechargeable battery capable of discharging to zero volts
without damaging the battery, said battery comprising:
20 a positive electrode and a negative electrode;
at least one of said electrodes being susceptible of permanent
damage when a voltage exceeding a Damage Potential Threshold (DPT) is
applied thereto;
said positive and negative electrodes defining a Zero Volt
25 Crossing Potential Threshold when the voltage between said electrodes is zero;
and wherein
said positive and negative electrodes are configured to define a
value of ZCP which is less than the value of DPT

30

11. The battery of claim 10 wherein said negative electrode comprises a metal substrate having a lithium based active material formed thereon, said negative electrode substrate being susceptible of permanent damage when a voltage exceeding a Substrate Dissolution Potential (SDP) is applied thereto;
5 and wherein
the value of SDP is greater than said value of ZCP.
12. The battery of claim 11 wherein said negative electrode substrate is formed of a material from the group titanium and titanium alloy.
10
13. The battery of claim 11 wherein said negative electrode substrate is formed of stainless steel.
14. The battery of claim 11 wherein said negative electrode substrate
15 is formed of a material from the group nickel and nickel alloy.
15. The battery of claim 11 wherein said positive electrode comprised a metal substrate having a lithium based active material formed thereon; and wherein
20 said positive electrode active material comprises a lithium-nickel-cobalt compound.
16. The battery of claim 11 further including an electrolyte; and wherein
25 said negative electrode can react to said electrolyte to form a solid electrolyte interface (SEI) layer, said SEI layer being susceptible of permanent damage when a voltage potential exceeding a Film Dissolution Potential (FDP) is applied thereto; and wherein
said positive and negative electrodes are configured to establish
30 ZCP at a lower level than FDP.

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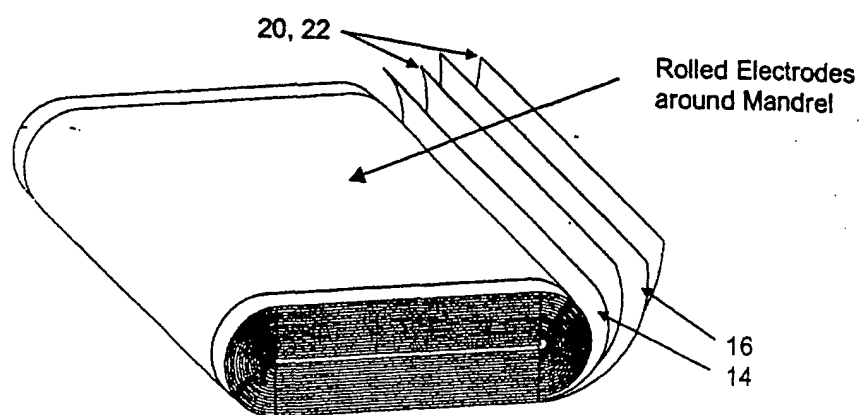


Figure 1A.

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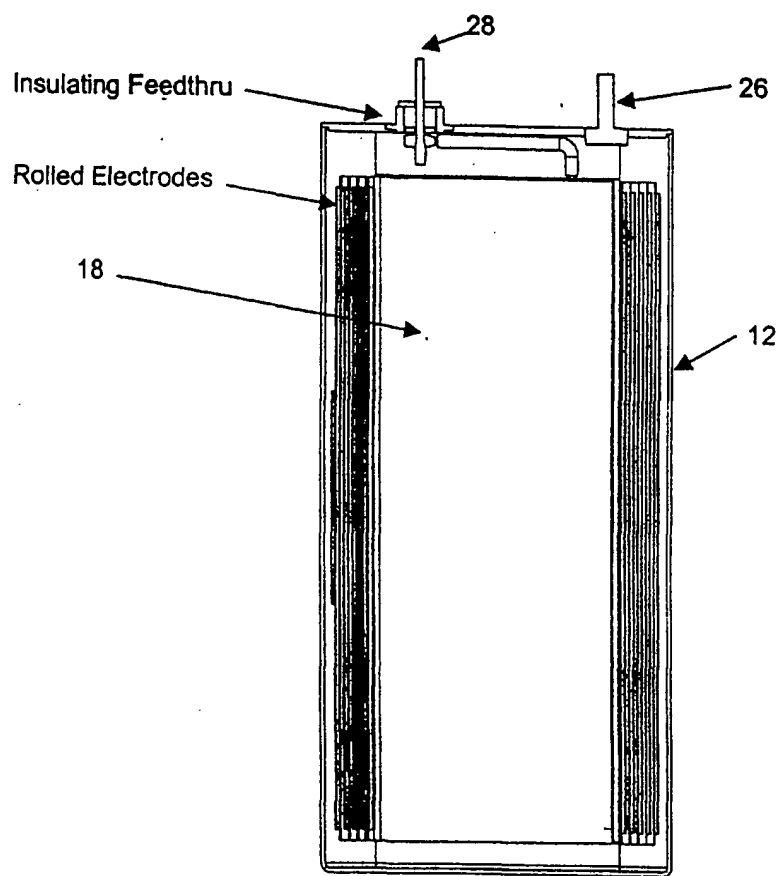


Figure 1B.

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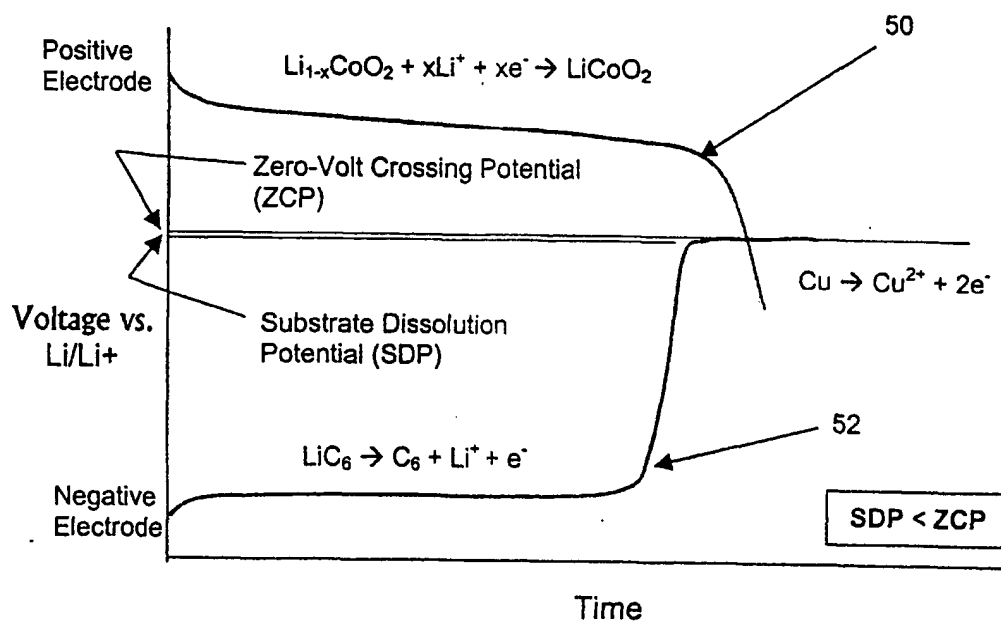


Figure 2.

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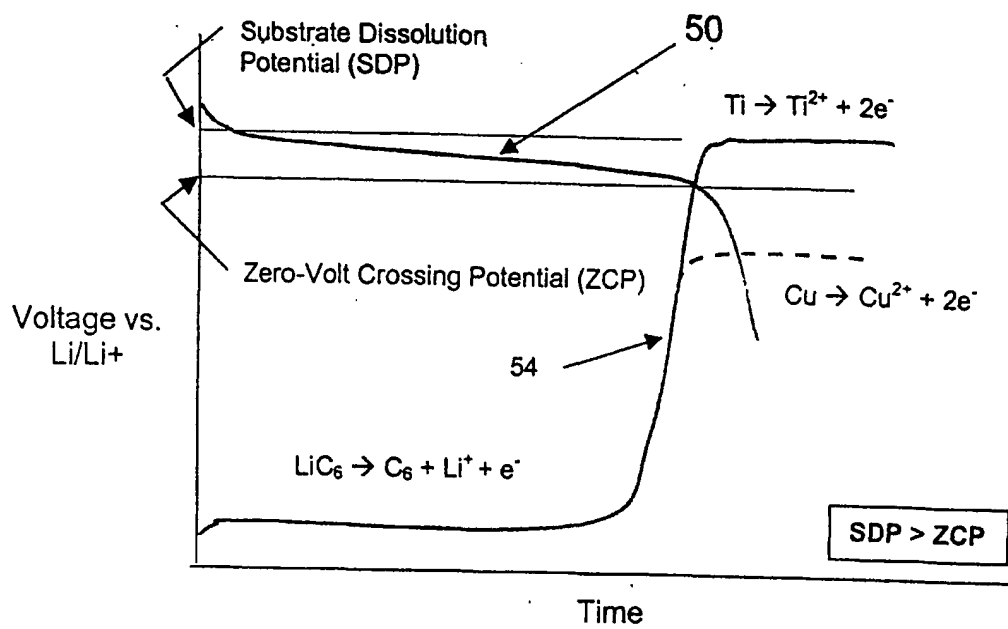


Figure 3.

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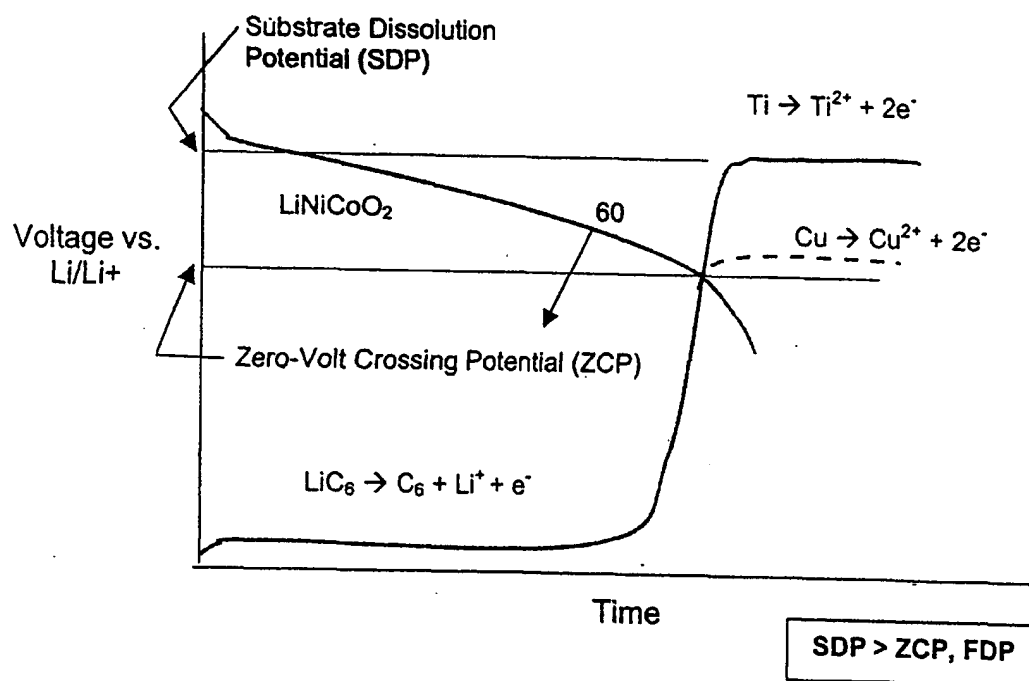


Figure 4.

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	Positive Active Material	Negative Substrate Material	Temperature	Result
(1)	LiCoO_2	Copper	25 °C	Fail; 79.9% Retention
			37 °C	Fail; 76.2% Retention
(2)	LiCoO_2	Titanium	25 °C	Pass; 98.6% Retention
			37 °C	Fail; 73.5% Retention
(3)	LiNiCoO_2	Copper	25 °C	—
			37 °C	Pass; 90% Retention
(4)	LiNiCoO_2	Titanium	25 °C	—
			37 °C	Pass; 98.8% Retention

Figure 5.

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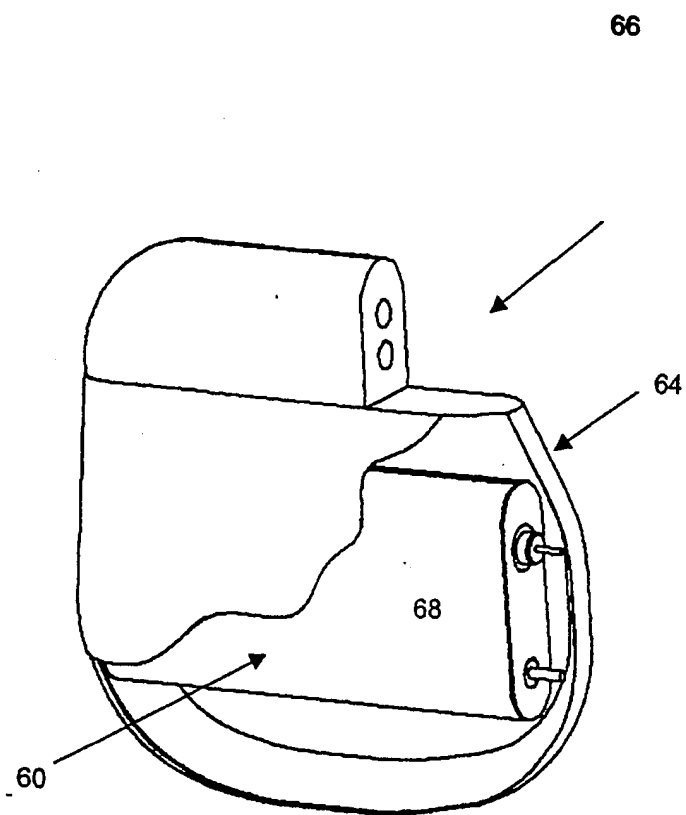


Figure 6.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US01/13308

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : H01M 4/66, 4/40, 4/52

US CL : 429/205, 233, 245, 231.95, 231.3, 223

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WEST 2.0 (US PAT, JP, EP AND DERWENT FILES)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US 5,631,100 A (YOSHINO et al.) 20 May 1997, claims 10, 14 and example 1.	1, 3, 4, 6, 10, 11, 13, 14, 16 ----- 7-9
X --- Y	US 5,264,201 A (DAHN et al.) 23 November 1993, see entire document	1, 5, 6, 10, 14-16 ----- 7-9
X --- Y	US 6,017,654 A (KUMTA et al.) 25 January 2000, claims 1-21.	1, 5, 6, 10, 11, 14-16 ----- 7-9

☒ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document published on or after the international filing date "L" document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed		"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "Z" document member of the same patent family
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Date of the actual completion of the international search

12 JULY 2001

Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US01/13308

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US 5,578,398 A (JENKINS et al.) 26 November 1996, claims 1-5.	1-4, 6, 10-13 ----- 7-9
X --- Y	US 4,092,464 A (DEY et al.) 30 May 1978, claims 1-12	1-3, 6-8, 10-13, 16 ----- 7
X ---- Y	US 5,783,333 A (MAYER) 21 July 1998, claims, table 3, col. 16, line 1.	1, 5, 6, 15-16 ----- 7-9
X,P	US 6,207,326 B (KAWAKAMI et al.) 27 March 2001, col. 46 and 89.	1, 2, 6, 10, 11, 16